

Sampling and Analysis Plan for  
Segment 3a Characterization  
San Juan County, Colorado

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Prepared for the Animas River Stakeholders group by William Simon

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## **Project/Task Organization**

The Animas River Stakeholders Group (ASRG) in cooperation with U. S. Geological Survey (USGS), Bureau of Land Management (BLM) and other participating stakeholders will coordinate the Segment 3a Characterization Project under a NPS 319 grant provided by the Colorado Water Quality Control Division (WQCD) provided to the San Juan RC&D. Bill Simon is the Watershed Coordinator for the ASRG. The BLM, BOR, FS, USGS, and SWWCD will also participate in associated activities indirectly related to Segment 3a characterization. Macroinvertebrate and water quality sampling will be done by trained personnel from member organizations of the ARSG. Samples will be analyzed by an EPA certified Lab. Results will be entered into the publicly-available database maintained by the ASRG, and into EPA's STORET database at the discretion and task of the WQCD. Because NPS 319 funding was withheld for nearly two years some project activities have already been accomplished including a low flow salt tracer, a high flow dye tracer, and a high flow salt tracer on Segment 3A between Arrastra gulch and Silverton.

## **Problem Definition/Background**

The discovery of gold and silver brought miners to the Silverton area in the early 1870's. The discovery of silver in the base-metal ores was the major factor in establishing Silverton as a permanent settlement. Between 1870 and 1890, the richer ore deposits were discovered and mined to the extent possible. Not until 1890 was any serious attempt made to mine and concentrate the larger low-grade ore bodies in the area. By 1900, there were 12 concentration mills in the valley sending products to the Kendrick and Gelder Smelter near the mouth of Cement Creek. Mining and milling slowed down circa 1905, and mines were consolidated into fewer and larger operations with the facilities for milling large volumes of ore. After 1907 mining and milling continued throughout the basin whenever prices were relatively favorable. By the 1970's only one year round producing mine (Sunnyside Mine) remained in the county. This mine ceased production in 1991, and has since undergone extensive reclamation efforts.

The Animas River and many of its tributaries above Silverton carry high concentrations of metals from both mining and natural sources. The ASRG and its member entities have undertaken extensive sampling to characterize the water quality of the upper Animas Basin, and prioritize locations where treatment could result in better water quality. The ARSG was responsible for assembling and analyzing all physical, chemical, and biological watershed information. They crafted the extensive Animas Use Attainability Analysis which was used to help the WQCC develop appropriate stream standards and TMDL's throughout the watershed. The adopted standards are based upon a combination of expected metal concentration reductions brought about by the remediation of 67 of the worse polluting mine sites and the biological potentials of the receiving streams.

During the 2001 Rule Making Hearing for stream standards on the Animas River it was recognized that Segment 3a, the Animas River segment between Minnie Gulch and Silverton, needed further characterization to determine specific sources of metal loading. The segment contains three mill sites, several tailings ponds, tailings on the river banks and tailings that are incorporated into the gravels within the flood plain. There are geological features that may be loading significant amounts of trace metals as well.

## **Project/Task Description**

This project will be focused on identification of trace metal sources to Segment 3a of the Animas River. This stream segment is monitored regularly by Colorado River Watch program (CRW) and the Bureau of Reclamation (BOR) at the stream flow gauge known as A68 at the segments lower end. Surface water sources have been characterized in the past without success of accounting for all the loading at A68. It is not certain if metal loading is coming from unaccounted for surface flows or from ground water contributions. Metals of concern are Cadmium, Copper, Manganese, Lead and Zinc. Water is at near neutral pH throughout the segment. Two fish surveys in the 1990's have been completed. A macroinvertebrate survey was completed and analyzed in 1997 from a fall sampling event in 1996 and a spring and fall event in 1997. Existing conditions were established at that time, summarized in the Animas Use Attainability Analysis, 2001.

This SAP is for the further characterization of Segment 3a of the Animas River, consisting of the following primary tasks:

1. Reconnaissance of surface water conditions (ARSG)
2. Tracer Investigations (BLM & USGS)
3. Surface and Ground Water Quality Analysis (ARSG)

Task 2 will be accomplished solely by independent ARSG participating entities (USGS & BLM) and therefore are not subject to this SAP; however the tasks are included to provide information on the integration of disciplines that will be used to accomplish Task 3 and ultimately reach decisions on source loading and the feasibility for remediation. The USGS tracer investigations are partially funded by the BLM. The USGS will use their own SAP for the investigations. .

**Task 1: Reconnaissance of surface water conditions (ARSG responsible entity).**

A reconnaissance to locate and measure physical parameters of all surface inflow on Segment 3a will be accomplished before high flow begins (this was completed in March, 2002) to determine if sources have been missed and to get an idea of the accuracy of previous physical parameter measurements. This may be repeated during a high flow event if access to the streams is possible.

**Task 2: Tracer Investigations (BLM and USGS responsible entities)**

A tracer study was completed in 1998 by the USGS for this stream segment. Although ground water sources were located, the event was done during low flow conditions but was complicated by a storm event. Recent surface water analyses

indicate that trace metal loading is most severe during high flow. Therefore a repeat study done at high flow is deemed desirable.

The USGS has agreed to do a repeat of the low flow tracer and a new high flow event. BLM has agreed to fund this investigation in cooperation with USGS. In the fall of 2001 USGS repeated the earlier 1998 salt tracer to provide additional data and to check to see if the 1998 tracer interpretations were accurate. In the spring of 2002 a dye tracer was completed to determine the transport speed of the water at high flow (rising limb of the hydrograph). This provided information on precisely when to sample the same parcel of water as it proceeded downstream during a follow up salt tracer. The salt tracer was then completed the next day. The results of the two dye tracers will be used to help locate significant surface and underground water sources of contamination. Analyses of the tracers will help focus future characterizations of these sources. (Incomplete analysis as of May 30, 2004).

### Task 3: Surface and Ground Water Quality Analysis

Following preliminary analysis of the tracer results water quality sampling will become focused on specific sources of metal exceedances. Surface water samples may be taken at the mouth of several inflows into the mainstem of the Animas River. Flows will be recorded whenever possible but many cannot be determined at high flow due to the large volume and heavy snow covering at that time of year. All water samples will be sent to an EPA certified laboratory for analysis. Filtering (Attachment 5) and flow (Attachment 6) protocols are included as attachments to this document.

There are several shallow (<40') wells that have been developed in the Animas floodplain throughout Segment 3a. These wells will be periodically sampled for water quality parameters that may further characterize the condition of the water as well as potential sources. More wells may be developed in areas of springs and seeps in order to characterize their water. Areas where these wells may be developed are included in the list of locations that may be sampled. Attachment 7 provides the groundwater sample collection procedures. Seep and springs entering the Animas river may also be sample using similar procedures outlined in Attachment 7.

In addition, wells, springs, and seeps may be sampled and analyzed for Chlorofluorocarbons (CFC) in order to determine the approximate age of the water. This could help better define probable sources of contamination. Attachment 7 provides the sample protocols for CFC's. Wells with plastic casings or screens cannot be sampled in this fashion.

## Data Quality Objectives for Measurement Data

The objective of this study is to determine sources and magnitude of loading of metals to Segment 3a of the Animas River.

## **WATER QUALITY**

Water quality sampling will involve the same protocols and analyses as previous sampling in Segment 3a to ensure comparability.

Precision and accuracy for dissolved metals are controlled by the field sampling technique and laboratory procedures. Precision will be evaluated by submitting blind duplicate samples for every 20 samples or less. Accuracy will be evaluated submitting a blank sample for every 20 samples or less to the laboratory. Selection of a certified lab will help insure analytical precision and accuracy.

Water quality sampling will be concentrated in areas known to be or determined to be significantly exceeding water quality standards.

The higher the frequency of sampling the better the data set is for characterizing a stream. However, it is known that the majority of metal loading comes with the high flow event. Therefore sampling will concentrate on those seasonal sources of loading.

Water quality samples from wells will be treated similar to those from surface water sources. Samples will be taken opportunistically, mostly at low flow conditions since the springs and seeps are usually inundated at high flows.

## **TRACER INVESTIGATIONS**

The tracer investigation objectives are to further determine surface and ground water sources of loading and their respective quantifications, where possible. These investigations will be accomplished by the USGS.

## **Sampling Process Design/ Sampling Methods Requirements**

### **WATER QUALITY**

#### *SURFACE WATER*

Wherever possible, water quality samples and flow measurements will be taken at locations such that significant in-flow metal contributions can be bracketed. Water quality samples and stream flow data will be used to characterize the concentrations, loads, and seasonal distribution of metal concentration exceedances throughout the stream segment.

Sampling will progress from downstream to upstream locations to eliminate sediment disturbance in subsequent samples. Surface water samples will be collected by immersing the sample bottle several inches beneath the water surface with the mouth of the sample bottle facing upstream. A separate surface sample may be collected if immiscible fluids are observed. To collect such a sample, the sample container will be

inverted, lowered to the approximate sample depth and held at about a 45-degree angle with the mouth of the bottle facing downstream.

If surface water samples cannot be collected directly into the sample container, a decontaminated 1 liter bottle will be used to collect the sample. The bottle will be rinsed three times in the water to be sampled prior to collecting the sample. Care will be taken to avoid excessive agitation when transferring samples to the sample containers.

Water samples for dissolved metals analysis will be field filtered with a 0.45 micron filter into the sample container and then preserved at a pH of 2 with nitric acid. Water samples for total metals analysis will not be filtered, but will be preserved at a pH of 2 with nitric acid. A non-filtered, non-acidified sample may be collected for anions.

Filtration will be done in accordance with "Standard operating procedures for the filtration of water samples" from the Quality Assurance Project Plan for the Colorado Nonpoint Source Monitoring Program (attachment 4); or with the following modification: Disposable encapsulated .45 micron filters (Gelman Sciences ion chromatography arcodisc or similarly approved disposable filter) may be used in place of the filter in the Swinnex filter holder. In this case, filters are rinsed with approximately 10 ml of the water to be sampled before the sample is collected. If the filter clogs, a new disposable encapsulated filter will be used. The new filter will also be rinsed with approximately 10 ml of the water to be sampled before continuing with the sample collection.

In-field measurements of pH, conductivity, and temperature, flow will be made for all water samples and field reconnaissance. Manufacturer's instructions for calibration and measurement of pH and conductivity will be followed. Type of meter will be noted on the field sheet. Flows will be taken using BASKI 1", 2" or 4" flumes, or appropriate current meters. Flow measurement will be in accordance with the "Standard operating procedures for the collection of flow, pH, temperature and conductivity measurements" from the Quality Assurance Project Plan for the Colorado Nonpoint Source Monitoring Program (attachment 5).

Measures will be taken to minimize the amount of in-field equipment decontamination required for the sampling event. Reused sampling equipment will be decontaminated prior to the sample event. Decontamination will be achieved by washing with an acid rinse and triple rinsing with de-ionized water. Field equipment will be decontaminated by triple rinsing in the field.

#### *GROUND WATER SAMPLING*

Ground water samples from springs and seeps will be taken whenever co-mingling of surface water can be avoided. A hole will be constructed in advance of sampling in which ground water may collect. Care must be taken to avoid sediment contamination; therefore sampling will take place only after all visible sediments have had time to settle out. Small seeps may be sampled by syringe or tubing if it can be done so as not to

introduce sediments. The filtering procedure and measurement procedure of pH, conductivity, and temperature filtering will follow those outlined above for surface water.

Sampling of wells will follow the procedures provided in Attachment 6. Wells with plastic casing and/or screens cannot be used to sample for CFC's.

## **Sample Handling and Custody Requirements**

Sample containers will be labeled with permanent marker or wax pencil directly on plastic bottles and on label tape on glass containers. The label shall contain the following sample identification information:

Waterbody - name and station number.

Date

Samplers initials

Remarks - special processing such as filtration, split sample, etc.

Time of day.

Sample preservation – (HNO<sub>3</sub>)

Sample Type: Filtered or unfiltered metals, chloroflorocarbons, anions, sulfur isotopes.

Filtered and unfiltered samples from a single site, along with a copy of the field data form, will be kept together in a plastic zip lock bag. Immediately after collection, samples will be kept in a cooler with ice at all times until they are transferred to the laboratory refrigerator, or sent to be analyzed. Samples must not be allowed to freeze. The necessary sample field documentation will be filled out on site (date, time, sampler, site, sample number and type) on the Animas River Field data form (attachment 1). Water Quality Data - Stream Sample sheet (attachment 2) will be completed for those samples to be submitted to an EPA approved laboratory for analysis.

Sample custody consists of two components: documentation and actual physical custody of the official sample. Physical custody consists of two phases: custody in the field and custody in the laboratory. Sample custody is less stringent for characterization and Best Management Practices monitoring than it would be for samples collected for enforcement or standards setting.

The following principles apply to all handling of samples from the point of collection through the placing of a sample in a secured location at the laboratory. The sample is considered in "custody" if:

1. It is in one's actual physical possession or view.
2. It is in ones physical possession so as not to be tampered with, i.e. under lock and restricted key or under official seal.
3. It is retained in a secured area with restricted access.



4. It is placed in a container and secured with an official seal(s) evidence tape such that the sample cannot be reached without breaking the seal(s).

Chain-of-custody form supplied by the lab, [and containing the same elements as the chain of custody form in "Standard operating procedures for field samplers" from the Quality Assurance Project Plan for the Colorado Nonpoint Source Monitoring Program (attachment 3)] will accompany the cooler from the sampling site to the lab.

### **Analytical Methods Requirements**

Analytical methods to be followed in this study are listed below. The methods used are described in EPA Region VIII's standard operating procedures. Any problems with the analytical methods that may be encountered during the study will be reported to ARSG and addressed by the laboratory technical manager.

Group	Constituent	Units of measurement	Reporting Limit *	Preservative	Field Filtration	Holding time	EPA analysis Method number	Container type
Field parameters	Temperature	mS/cm	1	--	None	Field analysis	1201	In situ or field container
	Specific conductance					Filed		
	pH	--	0.01	--	None	analysis	150.1	In situ or field container
Anions	Sulfate	mg/l	1.0	None	None	28 days @<4' C	300	500 mL polyethylene
Trace metals	Aluminum	µg/l	40.	2ml HNO <sub>3</sub> /liter	0.45 µm	6 months	200.7	1 liter polyethylene bottle, acid rinsed
	Arsenic	µg/l	1.	2ml HNO <sub>3</sub> /liter	0.45 µm or none	6 months	200.9	1 liter polyethylene bottle, acid rinsed
	Iron	µg/l	5.	2ml HNO <sub>3</sub> /liter	0.45 µm	6 months	200.7	1 liter polyethylene bottle, acid rinsed
	Cadmium	µg/l	0.5	2ml HNO <sub>3</sub> /liter	0.45 µm	6 months	200.9	1 liter polyethylene bottle, acid rinsed
	Copper	µg/l	0.8	2ml HNO <sub>3</sub> /liter	0.45 µm	6 months	200.9	1 liter polyethylene bottle, acid rinsed
	Lead	µg/l	0.8	2ml HNO <sub>3</sub> /liter	0.45 µm	6 months	200.9	1 liter polyethylene bottle, acid rinsed
	Manganese	µg/l	1.	2ml HNO <sub>3</sub> /liter	0.45 µm	6 months	200.7	1 liter polyethylene bottle, acid rinsed
	Nickel	µg/l	5.	2ml HNO <sub>3</sub> /liter	0.45 µm or none	6 months	200.7	1 liter polyethylene bottle, acid rinsed
	Zinc	µg/l	4.	2ml HNO <sub>3</sub> /liter	0.45 µm	6 months	200.7	1 liter polyethylene bottle, acid rinsed
Chloroflouro-carbons	CFC			none	none	2 months		250 ml. glass bottle w/foil cap; taped

\*Reporting limits for metals vary depending due to variations in sample matrix and individual laboratory abilities. The reporting limits listed above will be used as guidelines and attempts will be made to have these limits met as nearly as feasible.

## **Quality Control Requirements**

Sample bottles will be purchased commercially, will meet EPA specifications, and will be part of the quality control program. The sample containers to be used for this project will be 250 milliliter polyethylene bottles for surface water and other aqueous source samples (total recoverable metals, dissolved metals, and anions), except for sampling for CFS's in which case the bottle will be glass with foil lined screw top lids.

The following types of samples will be provided for QA/QC purposes:

Field blanks will be prepared for each group of sampling at the rate of one per 20 samples.

One duplicate water matrix water sample will be collected per 20 samples shipped to determine accuracy and precision in laboratory, analytical procedures and sample collection procedures.

One triple volume sample per 20 water samples can be collected, if the State's lab so requests, to provide matrix spike and matrix spike duplicate (MS/MSD) to allow for a check of laboratory quality control procedures.

One de-ionized water blank will be taken from the source of DI water which will be used for all equipment decontamination rinses.

Field blanks, and duplicates will be submitted with separate sample ID's as blind samples. Any triple volume samples gathered will be designated as being for Lab QC purposes.

## **Instrument Calibration and Frequency**

Field pH and conductivity meters will be calibrated at the beginning of each sampling day according to the manufacturer's specifications. Meters will be checked periodically during the day, with particular attention being given to re-calibration when temperatures change significantly, and when the character of the water changes significantly (eg., draining adit vs. stream water.)

## **Inspection/Acceptance requirements for Supplies**

Pre-cleaned, and pre-preserved sample bottles are obtained from ESS (Environmental Sampling Supply) or supplied by the selected laboratory. Filters for 0.45 micron filtration are ion chromatography arcodiscs obtained from Gelman sciences. Bottles and filters will be inspected before use, and any that have been damaged during shipment will be discarded to a location where they will not be inadvertently reused.

## **Data Acquisition Requirements**

The Segment 3a characterization study will be relying upon additional information supplied by CDOW (Riverwatch program), BOR and USGS (stream gauges and water quality data), and tracer studies (USGS). Data taken elsewhere in the Animas basin, to which this data will be compared, were collected using the protocols specified in the "Animas River Stakeholders Group Sampling and Analysis Plan, Animas River Characterization Project, San Juan County and La Plata Counties, Colorado, 1998." The protocols between that SAP and this one are similar, and should yield data that are valid for comparison.

## **Data Management**

Field data sheets will be kept by ARSG. Lab analysis results will be transcribed into the master database (an Excel database) maintained by the Animas River Stakeholders Group, Bill Simon, Watershed Coordinator; and eventually into EPA's STORET database at the discretion and task of the CDPHE.

## **Assessment and Response Actions**

Interim reports of progress and results of this characterization study will be given at Animas River Stakeholders Group monthly meetings. Any concerns about data collection procedures will be resolved by the Group at that time.

All field and laboratory activities may be reviewed by state and EPA quality assurance officers as requested. Results of this project will be included in a report to the Colorado Non-Point Source (319) Program, the ARSG and its participants, the WQCD, and the WQCC at the next scheduled triennial review and/or rule making hearing.

## **Data Review, Validation and Verification Requirements**

Interim reports of progress and results of Segment 3a characterization, including additional tracer and water quality analysis, will be given at Animas River Stakeholders Group monthly meetings. Any concerns about accepting, rejecting or qualifying the data will be made by the Monitoring Working Group to Bill Simon who is in charge of data management.

## **Validation and Verification Methods**

Analytical results will be compared to prior data at the same locations, and also to streams in the vicinity. Outliers or nonsensical data should be obvious, given the wealth of characterization data in the Upper Animas basin. If errors are detected, transcription errors from field or lab sheets will be checked, and quality control analyses will be reviewed. Data entry errors will be corrected. Inconsistencies will be flagged for further review, or discarded. Any problems with data quality will be discussed by the Monitoring Working Group and recommendations made to Bill Simon, data manager.

## **Reconciliation with data quality objectives**

The objectives of this characterization study are to determine source and magnitude of metal loading in Segment 3a of the Animas River. Depending on the complexity of the geochemical situation encountered, it may take several years of data collection to adequately characterize the metal sources. Other tributaries of the Animas River and stream segments have undergone similar characterization of its contamination sources. One always wants more data, but those existing data sets on the other tributaries and segments have been adequate for source analysis and recommendation of standards. The procedures described here will hopefully be adequate to generate a similar recommendations for modifying stream standards, TMDL's, and remediation of contaminating sources. .

## **ATTACHMENTS**

<b>Attachment 1</b>	<b>Animas River Field Data Form</b>
<b>Attachment 2</b>	<b>Field Sample Record</b>
<b>Attachment 3</b>	<b>Chain-of-Custody Form</b>
<b>Attachment 4</b>	<b>SOP for Filtration</b>
<b>Attachment 5</b>	<b>SOP for Flow Measurement</b>
<b>Attachment 6</b>	<b>Ground Water Sample Procedures</b>
<b>Attachment 7</b>	<b>CFC Sampling Method</b>
<b>Attachment 8</b>	<b>List of Potential Sample Sites</b>

**Attachment 1**  
(to be included in hard copy document)

**Animas River Field Data form**

**Attachment 2**  
(to be included in hard copy document)

**Field Sample Record**



### **Attachment 3**

### **Chain-of-custody form**

Chain of custody forms are supplied in advance of shipping by the laboratory to be used. Request the form and fill out as per instructions. Keep copy and send copy along in ziplock baggie along with samples.

## **Attachment 4**

## **SOP for filtration**

from "Standard operating procedures for the filtration of water samples" from the Quality Assurance Project Plan for the Colorado Nonpoint Source Monitoring Program (attachment 4

In 1988, the Colorado Water Quality Control Commission adopted the determination of metals concentrations in surface waters be based on the dissolved fraction rather than the acid soluble or total recoverable method used previously. This was based on EPA's acute and chronic criteria which, in most cases, are equations that calculate the metals standard for a stream segment for aquatic life protection. (McConnell-Dissolved Metals monitoring-1988). The Aquatic Life criterion is based on the dissolved metals and the total hardness concentrations.

Dissolved metals concentrations are used to develop water quality standards, nonpoint source controls, to calculate loadings, and to develop remedial models. The methods described in this standard operating procedure document will focus on a "syringe" filter 'ing procedure, used in the field by NPS personnel in determining dissolved metals concentrations. Another common filtration procedure is the use of a Geotech filtration unit which is well documented in **McConnell's** Memo to-field samplers (Attached).

### **EQUIPMENT**

1. 60 cc syringe w/Luer-Lok tips.
2. Swinnex disc filter holders, 47 mm diameter, polypropylene with silicone O-rings.
3. Cellulose Acetate 47mm diameter, .45 um pore size filters.
4. Deionized water used for rinsing.
5. Teflon coated or nonmetal forceps.
6. Pre-acidified 250 ml bottles.
7. Precleaned and rinsed sample container. (1 liter bottle)

### **SITE AND SAMPLING CONSIDERATIONS**

Several considerations should be taken before an actual sample is obtained.

1. Make sure the area to be sampled is thoroughly mixed with any contributing inputs such as confluences with other streams, discharges, runoffs, mine adits, or any other water body contributor.
2. If more than one site is going to be sampled, each site should have it's own collecting and filtering equipment. This is not always practical where there are numerous sites to be monitored. In this case, 2 or more sets of equipment are used, one set at suspected contaminated sites, and one set for suspected clean sites. This technique reduces the possibility of contamination going from a highly polluted site to a relatively

clean site. If one set of collecting equipment is going to be used, sampling should progress from the clean areas to the contaminated areas. Thorough rinsing is the key to uncontaminated samples.

3. If sampling several locations on the same waterbody, a "downstream-to-upstream" approach is to be used. This ensures that any substrate constituents which may be stirred up during the sampling procedure are going to flow downstream as you work upstream and will not be introduced at the next station.

## **SAMPLE PREPARATION**

All sampling equipment must be cleaned and rinsed before any sample collection may take place. The Colorado Department of Health Laboratory supplies all sampling containers and preacidified 250ml metals containers which are cleaned under the laboratory's Quality Assurance Plan.

The filter holders and syringes must also be clean. Disassemble the filter holder apparatus. The O-rings on the upper and lower section of the holders are soaked in deionized water for 24 hours. The filter holders and syringes must be soaked in a 5% nitric acid, 95% deionized water mixture for 24 hours. Then rinsed with deionized water prior to use.

## **QUALITY ASSURANCE**

A duplicate sample will be collected at 10% of the sampling stations for QA purposes. The duplicate is taken out of the same container as the stream sample. Rinsing of the filter holder and a new filter are placed in the filter holder using the procedures described. The duplicate sample will be labeled "FILT DUP", along with the site name or number, date, time, and name.

A "BLANK" sample of the de-ionized water used in rinsing is taken at the end of each sampling day. The same rinsing and filtering procedure is used for the sample.

## **FILTRATION PROCEDURES**

1. Rinse a 1-liter neutral (unpreserved) container with the water to be sampled at least three times before gathering a sample to be filtered on-site or in a lab (camper-lab). Fill container and cap for later filtering. Filtering is done no later than a half an hour after collection.
2. Locate a dust free environment as possible, ideally, a mobile or camper lab to set up and filter.
3. Rinse the syringe and filter holder with de-ionized water.
4. Place a clean filter in the filter holding apparatus using non metal (clean and rinsed) forceps.

5. Run 50 ml of de-ionized water through the filtering apparatus using the syringe. Do not collect this.
6. Run 50 ml of sample water through the filtering apparatus using the syringe, again, do not collect this.
7. After being completely rinsed and flushed, the sample may be filtered into the pre-acidified container. Do not rinse the pre-acidified container. If the filter begins to clog, do not force the sample through the filter, but replace with a new filter after following the rinsing procedures.
8. Fill the sample container to the rim of the pre-acidified bottle. The container has a predetermined amount of preservative for a full sample.
9. Label bottle with the site, time, date and sample type, i.e. "Filtered", "Filt Dup", or "Filt Blank".
10. Immediately and thoroughly rinse all filtering equipment with de-ionized water before it dries and place in a zip lock storage bag for transport to the next site.
11. Upon completion of a sampling run, the filtering apparatus should be taken apart and soaked in a mixture of 5% nitric acid and 95% de-ionized water for 24 hours as described above.

## **Attachment 5**

## **Flow Measurement**

(from "Standard operating procedures for the collection of flow, pH, temperature and conductivity measurements" from the Quality Assurance Project Plan for the Colorado Non-point Source Monitoring Program)

### **FLOW MEASUREMENTS:**

#### **OVERVIEW:**

Discharge measurements are a vital part of water quality sampling. Discharge is used in constituent loading formulas, dilution factors, and discharge rates, as well as other aspects in which the rate of flow is needed. This Standard Operating Procedure will focus predominantly on instantaneous flow measurement procedures for open channels as needed in water quality sampling protocols.

#### **TYPES OF FLOWMETERS**

There are different types of flowmeters available for use, such as the Pygmy, Marsh-McBirney, and Price AA meters. Although they operate differently, they provide comparable results. Follow the individual unit's manufacturer's instructions.

#### **CALIBRATION SCHEDULE**

sampling personnel should calibrate their flowmeters at least once per year. The USGS or the local supplier of flowmeters should have a flume setup in which flowmeters may compare readings to the known flow of the flume, traceable to the National Bureau of Standards.

#### **QUALITY ASSURANCE USING DIFFERENT FLOWMETERS IN A STUDY**

In detailed and intense studies, in which many crews are involved, a quality assurance check should be done at the beginning of each sampling day to ensure that proper and comparable flow readings are being taken. This involves eliminating as many different factors as possible. Use of the same type of meter is ideal but not always the case. Steps to be taken include:

1. Taking flow measurements at an identical location.
2. Using the same cross section intervals.
3. Each crew shall use the same technique they are going to use in the field to collect their flow measurements.
4. Field notes and field forms should be the same or similar for use in the same study. (See attached discharge measurement form)
5. Final flow measurements should compare to within 10% of each other. Make any necessary adjustments and duplicate flow procedures until within 10%. (See discharge calculation section). Follow flowmeter's manufacturer's instruction manual. Marsh McBirney instruction manual attached.

#### **SELECTION OF STREAM SITE FOR FLOW READING**

Selecting a cross section of a stream or channel for flow measurement requires careful consideration.

1. Select a stretch in which the stream is not turbulent, or fluctuating from side to side. Preferably a glide type area.

2. Suspend a measuring tape, which is calibrated in feet and foot-tenths, one foot above the stream or channel, perpendicular to the flow.
3. Measurements will be made perpendicular to the flow, facing upstream. Measurements will be in feet/second.
4. If depth is less than 2.5 feet, the flow measurement will be taken at 60% of the depth, from the surface. This is the standard setting of the top setting rod. If over 2.5 feet in depth, a two point method is used, which is the average velocity at a 20% and 80% depth measurement. This is done by calculating the 20 and 80% depths and placing the electromagnetic sensor (Marsh-McBirney Model) on the top setting rod, at the distance from the surface.
5. Try to avoid areas where there are dead pools of water such as behind large boulders.
6. Take a minimum of 10 measurements within the stream channel, including distance from bank, depth, and velocity. The more segments you use the better the result. Also record the bank distances. (See flow data sheet attached). If the difference in velocity between two adjacent segments is greater than 10%, the segments should be smaller.
7. Follow the manufacturer's instructions for individual types of flowmeters.

#### DISCHARGE CALCULATION

Stream Profile:

W4    W5    wx

(in the hard copy document, stream cross section goes here)

45    Dx

where;

W    = Measured width of segment  
V    =  
A    = Calculated area of segment  
D    = Measured depth of segment  
Q    = Calculated flow of segment

= Measured velocity of segment

Calculate the area of each segment by:  $(Dx + D') / 2 * (Wx + Wx') / 2 = A'$  Calculate

the average velocity of the segment:

$$V_9 = (V_x + V_{x'}) / 2$$

Then calculate the flow of each segment by:

$$A_x \cdot v_x = Q_x$$

Sum the flow of the segments for the total flow.

$$Q_1 + Q_2 + Q_3 + \dots + Q_n = Q_{tt}$$

## Attachment 6

## Ground Water Sample Procedures

This section describes monitoring well locations, sample collection procedures and analytical parameters for the proposed groundwater monitoring events. Groundwater sampling events will be conducted during the low-flow (fall) and high flow (spring) surface water events and at other opportunistic times. Additional groundwater samples may be collected on a quarterly basis, pending adequate funding.

### *Monitoring Well Locations:*

Well locations are listing in Site Locations – Attachment 7.

Three to four additional shallow monitoring wells may be installed in the Animas River floodplain, between Arrastra gulch and the Town of Silverton following completion and analysis of the USGS/BLM tracer investigations.

### *Sample Collection Procedures:*

Each groundwater monitoring well will be sampled during or after high flow and during the low flow regime. Groundwater field data collection procedures will consist of water level measurements, measurements of field water quality parameters, and collection of samples for laboratory analyses. Before collecting a groundwater sample, the well number, current and previous weather conditions, field personnel, and the sampling date and time will be recorded.

Listed below are general preparatory steps followed by subsections on specific measurements and analyses.

1. Lay clean plastic sheeting around the well to minimize likelihood of contamination of equipment from soil adjacent to the well.
2. Remove locking well cap, note location, time of day, and date on well sampling sheet.
3. Remove well casing cap.

### *Water Level Measurements:*

Prior to sample collection, the depth to water in each well will be measured and recorded on the Groundwater Sampling Record – Attachment 9. Water levels in all wells will be measured within a short time period to minimize the potential effect of short-term fluctuations. All measurements will begin from the upper lip of the well head pipe. The water level measurement will be made from the designated measuring point with a water-level instrument. Both depths to water and total well depth will be measured. All water-level measurements will be recorded to the nearest 0.01-foot. The volume of water in each monitoring well will be calculated based on the depth to water, total depth, **and diameter of the well. The well water volume will be recorded on the Groundwater Sampling Record.**



#### *Well Purging and Field Measurements:*

Three to five well volumes will be purged from each well prior to the collection of samples. Wells will be purged and sampled using a disposable PVC bailer, peristaltic pump, or other suitable apparatus, depending on the rate of yield from each well and sediment load in the purge water. Samples taken for CFC analysis will use only Viton or Butyl N tubing and a peristaltic pump. Temperature, pH, and conductivity, and dissolved oxygen (if available) will be monitored during the purging process and recorded on the Groundwater Sampling Record – Attachment 9. Protocols for the measurement of field parameters will be identical to those for Surface Water Sampling found elsewhere in this Sample and Analysis Plan. Field measurements and groundwater samples will not be collected until these parameters have stabilized (i.e. +/- 10%), and a minimum of three well volumes have been removed from each well. If the well yield from any well is low and the well is purged dry, the well will be allowed to recover for up to 24 hours. If the well does not recover within a 24 hour period, the three volume minimum requirement will be waived and the well will be sampled using the second purge volume.

Groundwater sampling equipment (e.g. bailers, bailer cord, pump and pump tubing) that comes in contact with a groundwater sample will either be disposable, dedicated equipment which will only be used at one sampling location to prevent cross-contamination, or thoroughly cleaned with a nitric acid wash and triple DI rinse. Parameters to be analyzed in the laboratory will be the same as for surface water analysis listed elsewhere in this SAP.

Water discharging from springs and seeps will be sampled when the opportunity arises. Samples will either be withdrawn directly from the discharge source, as in surface water sampling procedures, or will be directed into a shallow, hand dug, holding pond. In this case, care will be taken to allow sediments to settle and several volumes of water to be replaced in the developed pool before sampling.

#### *Sample Collection for Metals Laboratory Analysis*

Sampling should be planned to collect groundwater samples from wells known or suspected to contain the lowest concentrations of trace metals first, finishing with the groundwater samples known or suspected to contain the highest concentrations. The following protocols should be followed to collect groundwater samples.

1. Preparation of bottles and labeling of bottles shall follow the procedures for surface sampling, including acidification of the dissolved metal bottles.

2. Ascertain that the pump, tubing, and receiving vessel, or any other apparatus, for the water sample has been acid rinsed and triple D.I. rinsed prior to drawing for the sample for lab analysis.
3. Well Purging and Field Measurements procedures listed above must be followed before lab analysis samples are taken.
4. Lower the bailer or end of the pump tubing slowly and gently into the well, taking care not to shake the casing sides or splash the bailer or tubing into the water. Stop lowering at a point adjacent to the screen.
5. Allow bailer to fill and then slowly and gently retrieve the bailer from the well, avoiding contact with the casing, so as not to knock precipitates or other foreign materials into the bailer. If using a pump, begin pumping water from the well.
6. Remove the cap from the sample container and place it on the plastic sheet or in a location where it won't become contaminated.
7. Slowly pour water from the bailer into a clean, pre-labeled sample container or into a 1 to 2 liter clean container for taking subsamples for the individual samples. The procedure is the same for using a pump and tubing.
8. The filtering procedure is identical for that used for surface water.

Note: If the sample bottles are inadvertently overfilled, dump the water, rinse the bottle with sample water, re-acidify bottle and fill the bottle with filtered sample water.

#### *Sample Collection for CFC Laboratory Analysis*

See CFC Sampling Method, Attachment 6 of this SAP.

#### **Laboratory Analytical Parameters**

Groundwater samples will be analyzed for the same laboratory analytical parameters as the surface water samples, with the exception of unfiltered metals and TSS since these need not be taken. Each groundwater sample will be analyzed in the laboratory for at least Cadmium, Copper, Manganese, Lead and Zinc. Other optional analyses may be DOC, alkalinity, sulfate, aluminum, iron, and fluoride. For the metals, only dissolved (filtered) fractions will be analyzed.

## **Attachment 7**

## **CFC Sampling Method (from USGS Reston CFC Lab)**

### **COLLECTION AND PRESERVATION OF WATER SAMPLES FOR CHLOROFLUOROCARBON ANALYSIS IN GLASS BOTTLES WITH FOIL- LINED CAPS**

**Reston Chlorofluorocarbon Laboratory  
May 8, 2003**

During the past several years, the Reston Chlorofluorocarbon Laboratory has been investigating methods of collection and preservation of water samples for chlorofluorocarbon analysis that can replace the present, somewhat labor-intensive, method of fusing water samples into borosilicate ampoules. A new procedure that involves filling and capping simple glass bottles with special foil-lined caps under water has been tested. Samples analyzed after storage over the past 6 months demonstrate the validity of the new method. This document describes the new sampling procedure and presents results of recent tests with the new CFC bottle method.

#### **CFC bottle method**

If archival of water samples for CFC or other VOC analysis for periods of more than 6 months is required, then it is recommended that water samples continue to be collected by fusing into borosilicate ampoules, as before (Busenberg and Plummer, 1992; [water.usgs.gov/lab/cfc](http://water.usgs.gov/lab/cfc)). Otherwise, water samples for CFC analysis can be collected in glass bottles capped with a special foil-lined cap, as described below.

#### **Source of bottles and caps**

Bottles and caps can be obtained from the SKS bottle company on the internet at URL [www.sks-bottle.com](http://www.sks-bottle.com). The bottles are 125ml (4 oz) boston round clear glass and have a cap size 22-400.

Item No. 40000040.01S is a case of 160 bottles with no caps.

Item No. 4000-04 is a case of 24 bottles with black cone lined caps. THESE BOTTLES HAVE THE WRONG CAPS! Discard these caps and replace them with the caps below.

Bottles are also available from any Wheaton glass supplier as Wheaton part number 217112, which is a case of 24 bottles with no caps.

The caps are sold as SKS item no. 6021-03, white metal caps with aluminum foil liner in a bag of 144. USE ONLY THESE ALUMINUM LINED CAPS! THIS CAP IS THE KEY TO THE METHOD. Discard any caps, if the foil liner appears scratched, dented, or altered in any way.

#### Filling procedure

**INSTRUCTION GIVEN BELOW MUST BE FOLLOWED TO THE LETTER TO OBTAIN GOOD RESULTS WITH THE BOTTLE SAMPLING METHOD FOR CFCs IN GROUND WATER.**

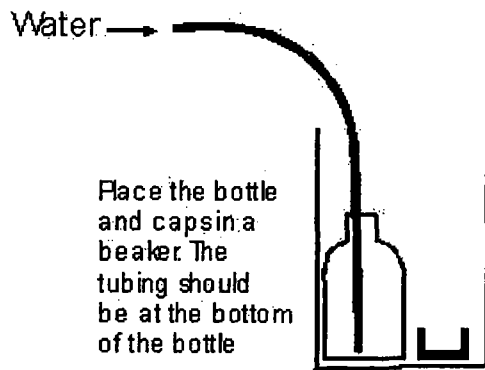
We are receiving too many samples with loose caps and caps that are not properly taped (see below for examples).

The bottles and caps should be THOUROGHLY rinsed with the ground water. The bottles are filled underwater in a beaker and capped underwater. Refrigeration-grade copper tubing (or Viton which has recently been approved for CFC sampling) is required, as previously used in the ampoule method. The filling procedure is carried out within a two to four liter beaker. A plastic beaker is fine. Collect 5 bottles per well or spring.

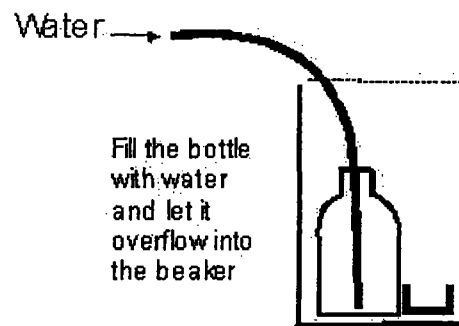
The procedure is shown below and is as follows (refer to the figure below) (do not sample from wells containing plastic screens or casings) :

1. After the well has been purged, place the bottle in the beaker and then insert the end of the copper tubing (or Viton) from the pump all the way into the **bottom** of the bottle. Also place all the caps (5 or more) in the beaker.
2. Fill the bottle as shown with well water until it overflows.
3. Continue to overflow the bottle until the beaker overflows. Allow at least 2 liters of water to flow through the bottle and out of the beaker.
4. Select a cap from the bottom of the beaker and tap it under water to dislodge air bubbles. Remove the copper tube from the bottle and **TIGHTLY cap the bottle underwater** without allowing the water in the bottle to come in contact with air. Flushing the bottle with more water is far better than with less water
5. Remove the capped bottle from the beaker, dry the bottle and **RE-TIGHTEN** the cap. The tighter the cap the better.
6. Invert the bottle, tap it and check it for air bubbles. If there are bubbles, repeat the procedure from step 2 above. If it is necessary to refill the bottle, you must use a new cap.
7. If there are no bubbles present, tape the cap **securely** to the bottle with **electrical tape**. Wrap the tape in a clockwise direction looking down from the bottle top. More than two rounds of electrical tape are needed. Do not forget to label each bottle with the well name, date, and time of sampling and the sequence number of each bottle as it was collected, one through five, in the order of collection.

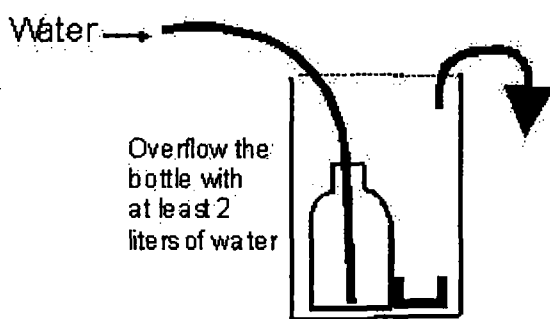
**USE ONLY THE METAL BOTTLE CAPS DESCRIBED IN THE TEXT ABOVE**



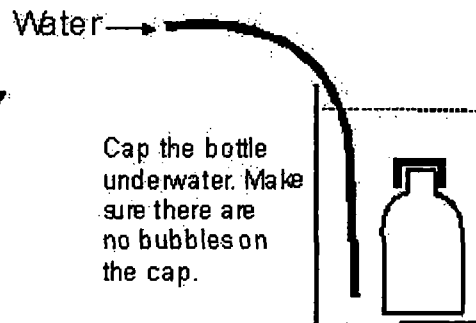
1



2



3



4

IF BUBBLES ARE PRESENT, REFILL BOTTLE - GO TO STEP 2.



5



6

Invert bottle and check for bubbles. If bubbles are **NOT** present, go to step 7.

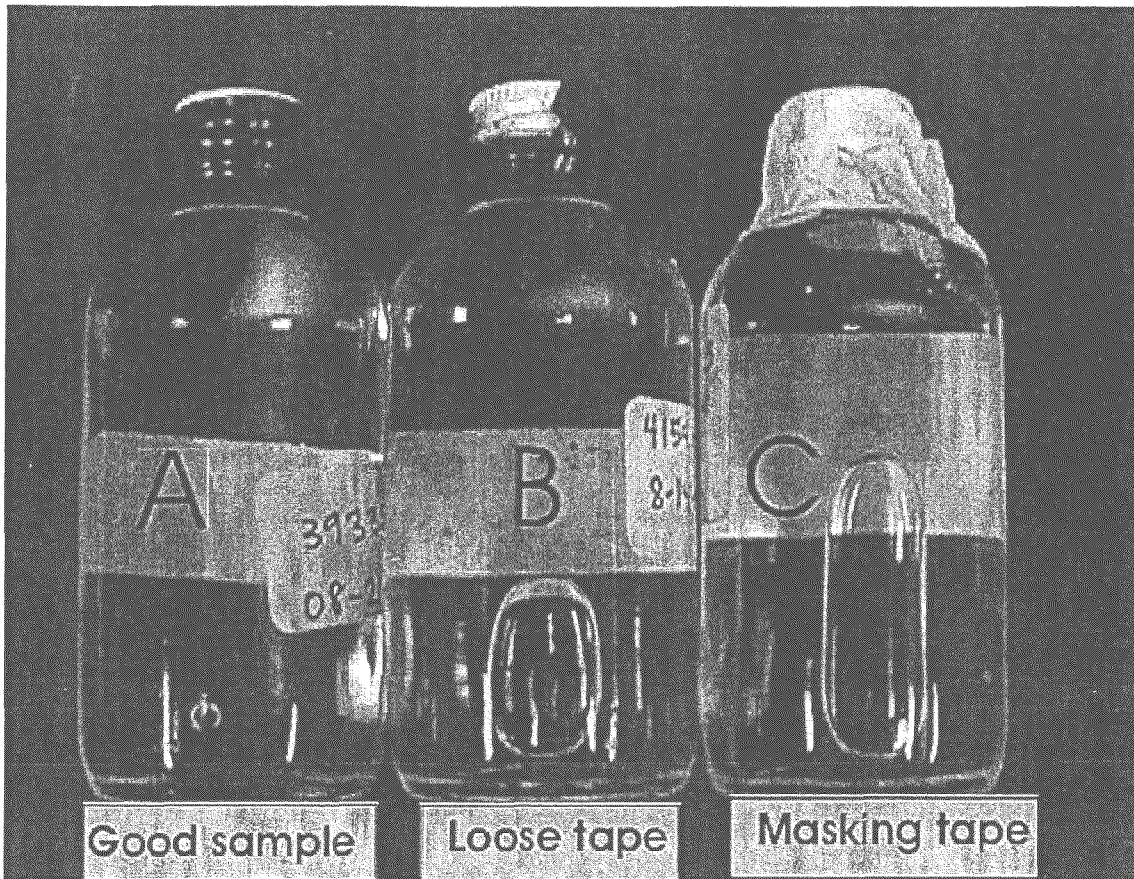


7

Tape the cap to the bottle

USE ONLY THE METAL BOTTLE CAPS DESCRIBED IN THE TEXT ABOVE

## Examples of properly and improperly sealed bottles



- A. Good example. Very tiny bubble formed.
- B. Poorly taped cap, air leak - note the large bubble that formed.
- C. Cap taped with masking tape, poor seal and large air bubble formed.

## Attachment 8

## Sample Sites and Locations

(All site are located within the Segment 3a watershed of the Animas River)

### SEGMENT 3A SAMPLE SITE LIST

#### GROUND WATER WELLS

Designation	Well in place	Site Description	Access Granted	Aliases	Lat	Long.	Elevation	Alias
GW-1	x	Campground Well	x	SV-2	37 49' 00' N	107 39' 44" W	9323	
GW-2	x	Well, Lion's Park	x	UV-1	37 49' 05" N	107 39' 39"W	9359	
GW-3	x	Well near sewer treatment plt.	x	SV-4	37 48' 12"N	107 40' 07"W	9249	
GW-4	x	Old Silverton Dump Well	x	SV-3	37 48'12" N	107 39' 44"W	9257	
GW-5	x	Silverton town well	x		37 48' 45"N	107 39' 33"W	9289	
GW-6	x	Power Plant Well	x	SGC-1	37 49' 22"N	107 38' 13"w	9434	
GW-7		Howardsville gauge well (USGS)	NA		37 50' 03"N	107 35' 54"W	9630	
GW-8	##	Howardsville well above POW tailings	x		37 50' 30"N	107 35' 24"W	9653	
GW-9	x	Heliport well	x		37 51' 14"N	107 34' 31"W	9723	
GW-10	x	Jepson's well	ask day of yes, through		37 51' 41"N	107 34' 16"W	9779	
GW-11	x	Boarding house @ Eureka	Fullmer	BH-1	37 53' 14"N	107 33' 44"W	9958	
GW-12	##	Behind mill ore storage pad	x		37 50' 12"N	107 35' 34"W	9703	
GW-13	##	East of mill ore storage area	x		37 50' 15"N	107 35'	9609	

GW-14	##	Adjacent tailing pond - east side near road	x	37 50' 21"N	31"W 107 35' 29"W	9652
G-1	X	POW - upstream of pond	x	37 50' 23"N	107 35' 33"W	9647
G-2	X	POW-between pond and Animas	x	37 50' 20"N	107 35' 41"W	9630
G-3	X	POW-downstream of pond area	x	37 50' 15"N	107 35' 44"W	9645

#### SPRING AND SEEPS

SP4300	small spring above pipe bridge
SP4353	spring level spring
SP4520	additonal spring on RB
SP4544	Algal pond below dry marsh
SP4806	Ab acid inflows
SP4916	T2->Blw acid inflows, ab Boulder Creek
SP5038	Substantial orange ppt. inflow
SP5131	Blw orange ppt tailings bin
SW5161	Pond to stream LB with fish

#### SURFACE WATER DIVERSIONS

D1	Diversion water around Mayflw. #4
D2	Diversion water around Mayflw. #1

#### SURFACE WATER SITES

CG-1	Campground surface discharge@confluence	37 48' 48"N	107 39' 24"W	9306
A35	Animas below Eureka Cr			
A40	Animas above Forest Queen trib.			
A41	Forest Queen			
A41A	Animas below Minnie			
A41B	Animas above Maggie			
LA-3	Animas below Maggie Confluence			

LA-1



A42	Minnie @ culvert	
A43	Maggie @ culvert	
A44	Hamlet Trib.@confluence	
A45	Animas above POW tailings	LA-4
A46	Old POW Tailings Seep	
A46A	Below A46 on Animas	
A47	Hematite @ confluence	
A48	Cunningham @ bridge	
A48A	Cunningham @ confluence	
A53	Animas above Howardsville bridge	
A53B	Animas below Cunningham	LA-5
A53C	Animas above Cunningham	
A54	Little Nation trib	
A55	Animas 1/4 mi. below A54	
	Animas above Arastra & Mill Overflow	
A56	pipe	LA-6
LA-6B	Animas above Mayflower diversion discharge	
A57	Animas-Mayflwr pipe	
A58	Arastra @confluence	AB-6
A60	Animas below Arastra	
A61	Animas above Boulder	LA-7
A62	Boulder @ confluence	BL-1
A63	Aspen trib @ confluence	
A63A	Aspen Mine	DM64
A64	Animas below Boulder & Aspen tribs.	LA-8
A65	Animas opposite Power House	
A66	Animas @ Lakawanna bridge	LA-9
A67	Swansea @ confluence	SW-1
A68	14th St. Gauge	

**Attachment 9**

**Groundwater Sampling Record Form**